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16. Abstract (Limit: 200 words)

Second Harmonic (SHG) and Sum-Frequency Generation (SFG) have enabled the investigation of the physical and chemical properties of aqueous interfaces, yielding new information and considerable insight into the structure and dynamics at a molecular level. Novel behavior has been observed and valuable new methodologies have been developed.

IR-Visible SFG has enabled the behavior of distinct chromophores within a molecular species at an aqueous interface to be monitored for the first time. An unexpected phase transition was observed at the liquid/vapor interface of aqueous solutions of acetonitrile. The structural change is manifested by shifts in the vibrational frequency and in the polarization of the SFG signal of the interfacial acetonitrile. This transition is analogous to those observed for monolayers of long chain amphiphilic species, also monitored for the first time with chromophore sensitivity. These results provide direct evidence that head and tail groups of amphiphilic molecules can orient independently, and a challenging picture of the nature of phase transitions in two dimensional molecular assemblies.

Electric Field Induced Second Harmonic Generation (EFISHG), a novel probe of charged interfaces, has been developed and applied to the study of the silica/aqueous interface and charged amphiphilic monolayers. Fundamental chemical quantities, such as the pKa of interfacial molecules, have been measured. In general, the interfacial acid-base equilibrium is shifted, with respect to the bulk, in a direction that favors the neutral species. Studies of the acid-base equilibrium of the silica/aqueous interface revealed two silanol sites whose acidity and thermodynamic parameters were determined.

Radiative electronic relaxation and the rotational diffusional motion of Rhodamine 6G at the air/aqueous interface were investigated. The ultrafast barrierless isomerization of an organic dye, Malachite Green, has also been probed with femtosecond time resolution, enabling the structure of water at various aqueous interfaces to be probed. In agreement with theoretical predictions, the solvent environment is more structured in the interfacial region than in the bulk.

This research has resulted in 17 publications and has been the subject of more than 30 invited talks, and has contributed to the training of 1 undergraduate and 6 graduate students as well as 4 postdoctoral fellows. 5 Ph.D. degrees were awarded during this period.

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Abstract

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I. Introduction

Liquid interfaces are notoriously difficult to investigate. For many years, measurements of macroscopic properties, such as surface tension and potential, were the only means of probing interfacial phenomena. Nonlinear optical spectroscopic methods, such as Second Harmonic Generation (SHG) and Sum Frequency Generation (SFG), developed in this laboratory and others have enabled insight on a molecular level with time resolution into the femtosecond regime ¹⁻³. These methods are inherently interface sensitive as SHG and SFG are dipole forbidden in bulk centrosymmetric media but allowed in the intrinsically asymmetric interfacial region. SHG and SFG can provide molecular level information on density, absolute and relative orientation, molecular environment with chemical and even chromophore specificity. Armed with these techniques, our studies have successfully addressed and answered a number of fundamental questions as detailed in this report.

II. Phase Transitions in 2-D molecular assemblies at the vapor/aqueous interface probed by IR+Visible Sum-Frequency Generation

Vibrationally resonant IR+visible surface Sum-Frequency Generation (SFG) has enabled the investigation, for the first time, of the spectral and structural behavior of both the head group and the tail of organic molecules at aqueous interfaces. Our spectroscopic and structural study of acetonitrile (CH_3CN) at the air/water interface using this technique found a sharp change of interfacial acetonitrile structure as a function of concentration, manifested by abrupt shifts in the CN vibrational frequency and orientation of acetonitrile molecules at the surface as indicated in Figure 1 ⁴.

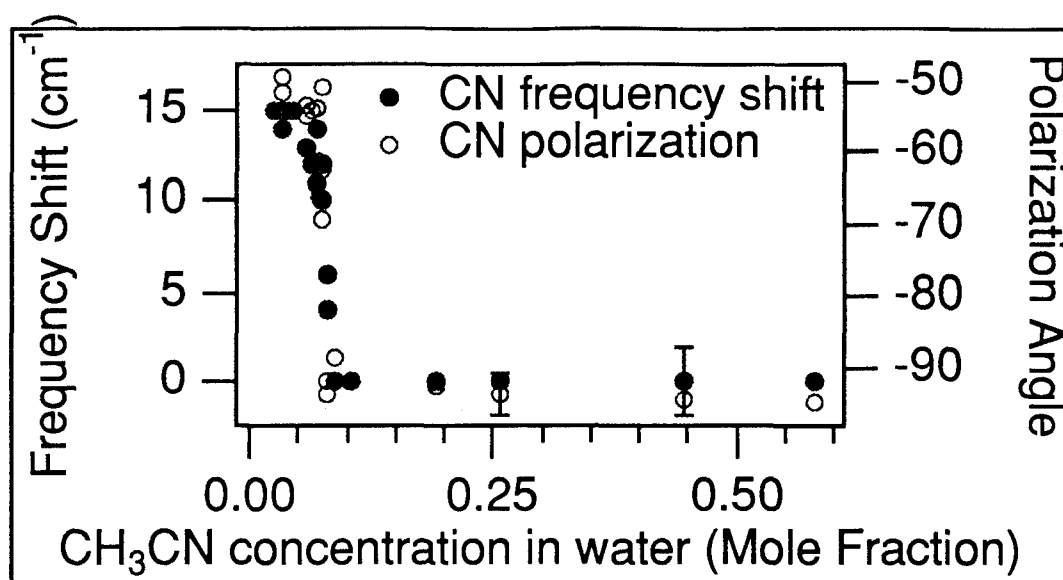


Figure 1. Interfacial CN vibrational frequency and Sum Frequency Polarization

We have investigated, also for the first time, both the hydrophilic head group (nitrile) and the hydrophobic tail (deuterated-methyl group) of a insoluble long chain amphiphilic monolayer (1-cyano-eicosane, $\text{CD}_3(\text{CH}_2)_{19}\text{CN}$) at the air/water interface⁵. Our results indicate that the orientations of the head and tail group of the amphiphile vary with surface density, but with markedly different dependence on density. As shown in Figure 2, the polarization of SFG from the CN (head group) remains constant throughout the gas-liquid coexistence region, as the intermolecular separation of molecules in the liquid density islands, the origin of most of the SFG signal, remains the same ($27 \text{ \AA}^2/\text{molecule}$). The orientation of the CN changes abruptly when the transition from the gas-liquid coexistence region to the liquid phase occurs, as molecules are squeezed to a density less than $27 \text{ \AA}^2/\text{molecule}$. The terminal methyl group behaves differently, as probed by SFG enhanced by resonance with the symmetric stretch. While no abrupt change in polarization is detected, the transition to the homogeneous liquid phase at the $27 \text{ \AA}^2/\text{molecule}$ is still observable as a change in the slope of polarization versus density curve for CD_3 , shown in Figure 3. We tentatively suggest that this gradual polarization change of SFG in the coexistence

region is due to the varying ratio of the number of molecules close to the perimeter of the liquid and gas phase regions to the number of molecules in the center of the liquid islands. Molecules close to the perimeter are more likely to have their tails extended in a more horizontal orientation towards the gas phase region, than molecules in the center of the islands, which should exhibit the more upright orientation of the liquid phase.

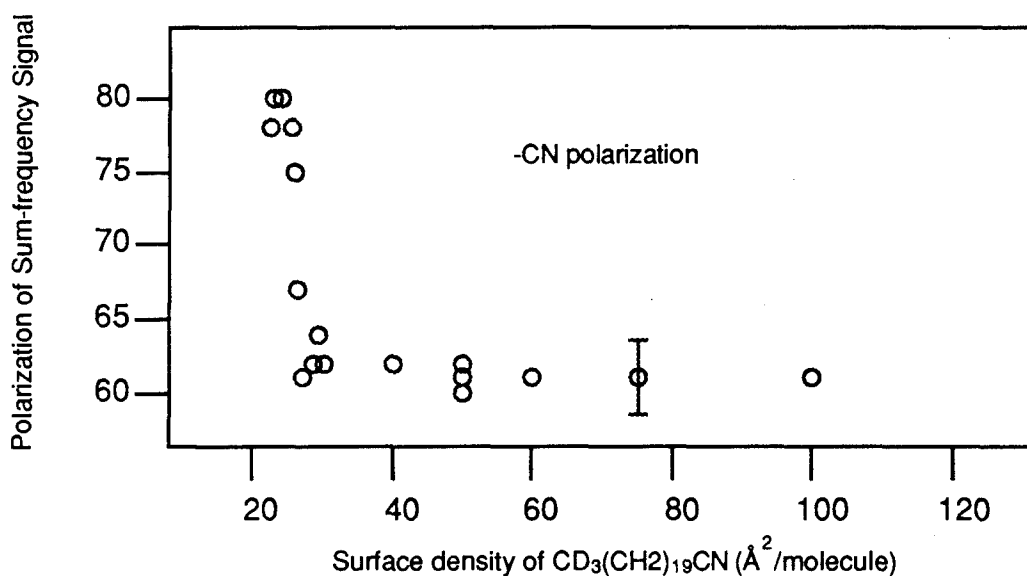


Figure 2. Polarization of SFG resonant with CN vibration of $\text{CD}_3(\text{CH}_2)_{19}\text{CN}$

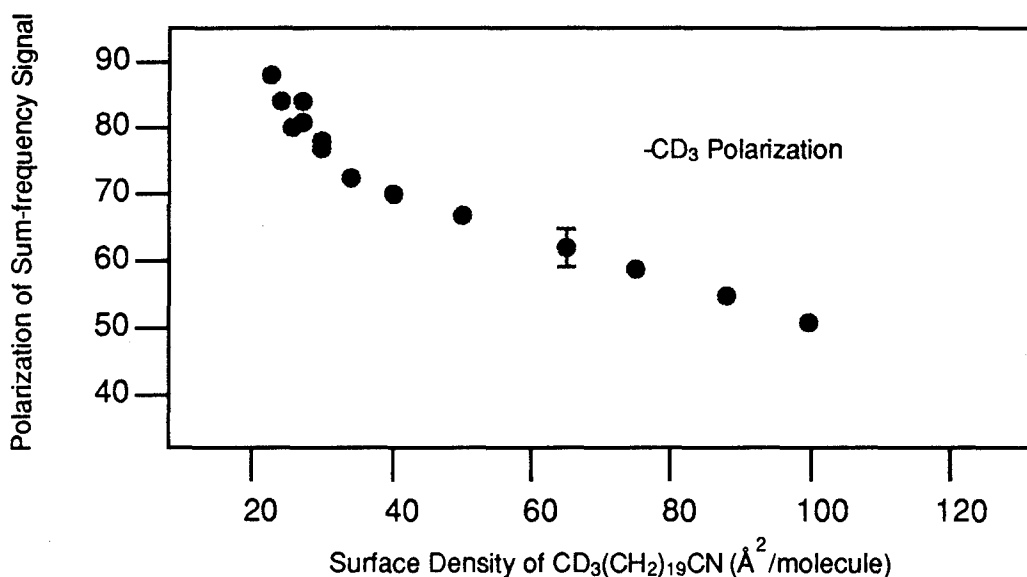


Figure 3. Polarization of SFG resonant with CD_3 vibration of $\text{CD}_3(\text{CH}_2)_{19}\text{CN}$

In addition, as manifested by a frequency shift in the CN vibration, our data indicate that the hydrogen bonds of water to the CN head groups are broken upon phase transition from gas-liquid coexistence region to the liquid phase region. This observation suggests that a key step in the phase transition requires that water molecules located between the nitrile head groups be squeezed out of the liquid phase monolayer. This conclusion is supported and generalized by additional studies of soluble aliphatic nitriles at air/water interfaces which show analogous frequency and orientational behavior. We tentatively propose that, contrary to the currently accepted picture of phase transitions in two dimensional systems at liquid interfaces, the driving force comes from the head group rather than the tail group of the molecules.

III: Charged interfaces studied by Electric Field Induced Second Harmonic Generation (EFISHG): The Silica/Water interface and long-chain amphiphilic monolayers at the air/water interface.

A novel probe of charged interfaces, Electric Field Induced Second Harmonic Generation (EFISHG), has been developed in this laboratory and has opened the way for the spectroscopic study of previously inaccessible interfaces. Surface Second Harmonic Generation (SHG), while interface specific, is inherently very weak because of the low density of species present in the interfacial region. SHG is enhanced, by at least an order of magnitude, when either the incident fundamental photons, or radiated second harmonic photons are resonant with a molecular transition. In the absence of such a resonance, SHG can be enhanced if the interfacial region, where bulk centrosymmetric order is broken, is increased. This occurs when interfacial charges orient bulk molecules in the near-surface region which then contribute to the SH signal through their third order nonlinear polarizability, leading to enhancements of SH signal of an order magnitude or more ⁶. EFISHG is proportional to the interfacial potential ⁷. EFISHG provides a novel means to study the interfacial potential and acid-base

equilibria at various interfaces, as well as the behavior of charged interfacial species which are not accessible by fluorescence or resonant SHG methods.

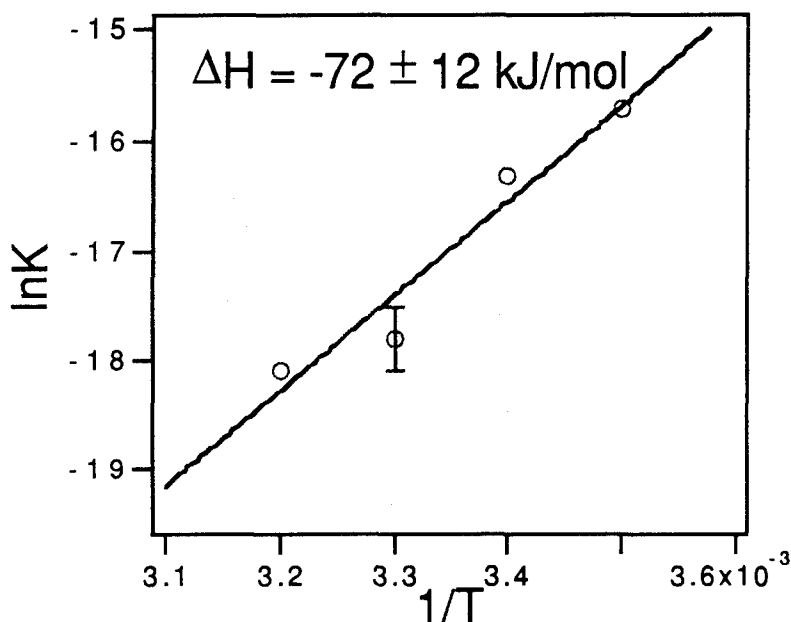


Figure 4. Temperature dependence of acid-base equilibrium constant of less acidic silanol site at silica/aqueous interface

We have applied EFISHG to the silica/water interface and determined the pK_a values for two different silanol sites of this interfacial acid-base system. Temperature dependent studies indicate that the pK_a of the more acidic silanol site is invariant from 283 to 313K. In the same range the higher pK_a is associated with $\Delta H = -72 \pm 12$ kJ/mol and $\Delta S = -384$ J/Kmol (Figure 4). To our knowledge, this is the first time that thermodynamic data on the fused silica/water interface have been obtained⁸.

EFISHG was also applied for the first time to investigate long chain amphiphilic molecular monolayers not accessible to study with the resonant SHG method⁹. EFISHG has enabled the surface pK_a of a number of amphiphilic monolayer systems to be investigated at different surface densities and on solutions of different ionic strength. In the case of the n-docosyl amine ($CH_3(CH_2)_{21}NH_2$) monolayer at the air/water

interface our experiment yields the same values of interfacial pK_a (10.2 ± 0.2) of $CH_3(CH_2)_{21}NH_3^+$ for various surface densities ranging from 100 to $22 \text{ \AA}^2/\text{molecule}$ ¹⁰. This pK_a value indicates that interfacial ammonium groups are more acidic than their bulk counterparts. The direction of this shift is consistent with our previous resonant SHG studies on long chain hexadecyl aniline, where the anilinium head groups is more acidic at the interface than in the bulk¹¹.

IV. Ultrafast Dynamics of Elementary Molecular Motion at Solid, Liquid and Vapor/Aqueous Interfaces by Time-Resolved Second Harmonic Generation

Time-resolved Second Harmonic Generation (SHG), by avoiding the complications of bulk contributions, enables the dynamics of surface species to be probed directly and on an ultrafast timescale¹²⁻¹⁴. Using this technique, progress has been made in our understanding of elementary molecular processes at interfaces¹².

The rotational motion of Rhodamine 6G, a large organic molecule, at the air/aqueous interface has been studied using picosecond SHG. The interfacial relaxation dynamics were observed to be slower than in the bulk, and dominated by out of plane motions¹³. Distinct polarization components of the SHG signal, which depend differently on molecular orientation, showed different time dependence shown in Figure 5. Indeed, upon photoexcitation one polarization component of the SHG signal (χ_{zxx}) was observed to decrease before increasing beyond the initial level associated with ground state Rhodamine 6G molecules. This suggests that the equilibrium orientational distribution of the photoexcited molecules differs from that of the ground state, and that excited molecules undergo rotation towards their equilibrium distributions in addition to relaxing back to the ground state.

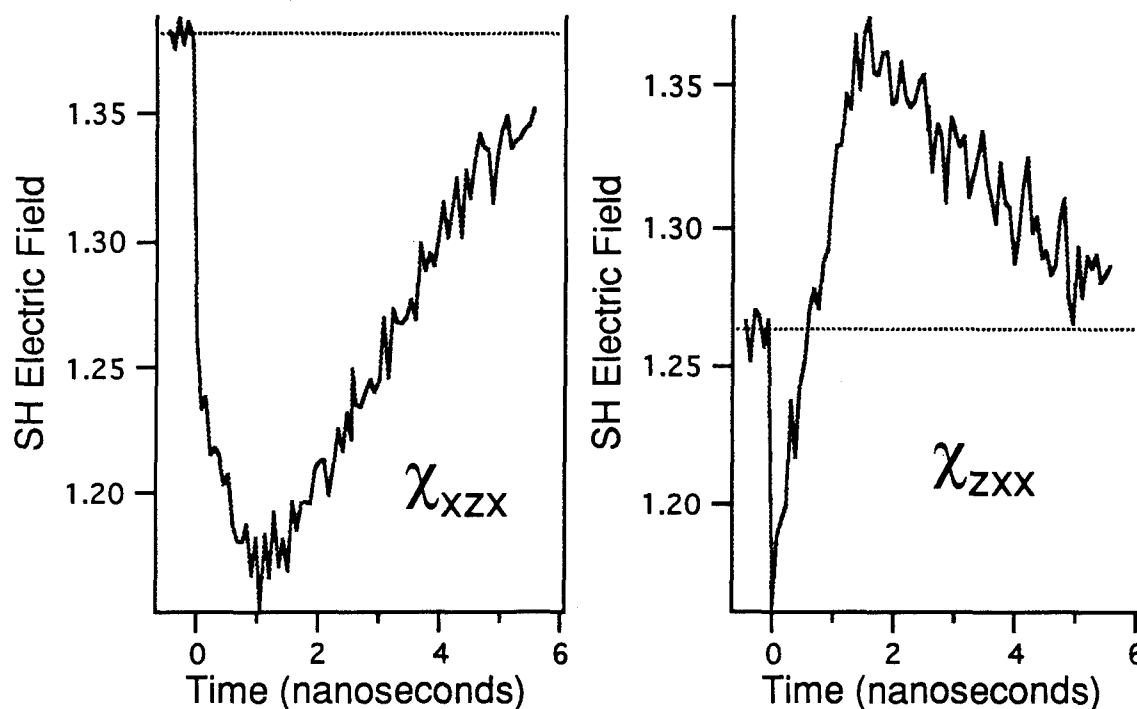


Figure 5. Time-resolved SHG of Rhodamine 6G at air/aqueous interface

Our results on the barrierless isomerization of an organic dye (Malachite Green) indicate novel and unanticipated behavior: a very large change in relaxation rates, slower by an order of magnitude (3.5-6.2 ps) from those in the bulk (0.7 ps) and surprisingly similar rates at very different interfaces, namely the air/liquid, liquid/liquid and liquid/solid interfaces (Figure 6) [12].

The natural tendency of molecules to orient at interfaces has been used, for the first time to our knowledge, to probe the contributions of different molecular moieties to the non-adiabatic electronic relaxation processes. Triphenylmethane dyes, such as Malachite Green, exhibit a strong dependence of fluorescence quantum yield and ground state recovery on solvent viscosity. The excited state relaxation process involves large amplitude motion of the phenyl rings, about the bond between each ring and the central carbon atom, against the resistance force of solvent viscosity. The hydrophobic part of

the molecule, the phenyl group, should be pointed away from the aqueous phase and the more hydrophilic part, the partially charged dimethylaniline groups, are expected to be oriented into the aqueous phase. The air vs. the pentadecane phase should offer very different frictional resistance to the twisting of the hydrophobic phenyl group. The similarity of the observed relaxation rates, 3.5 ps and 3.6 ps for the air/aqueous and pentadecane/aqueous interfaces respectively, indicates that the photoisomerization dynamics of Malachite Green do not significantly depend on the rotation of the phenyl group. Thus the interface and surface SHG can be combined to better understand bulk relaxation processes.

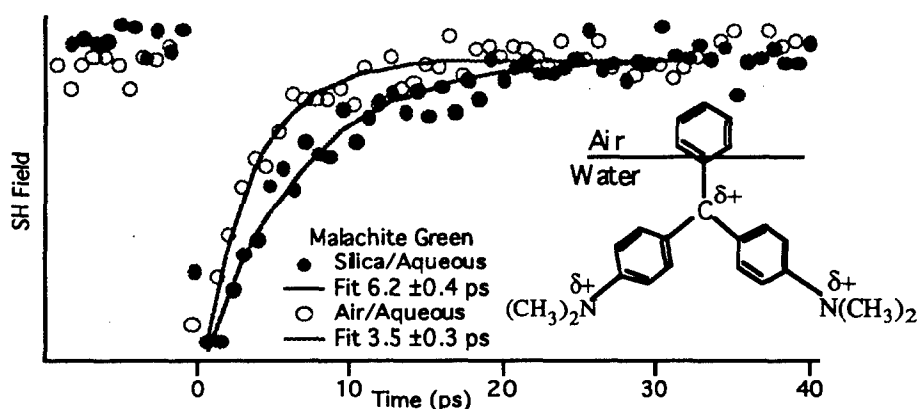


Figure 6. Time-resolved SHG of Malachite Green at air and silica/aqueous interfaces

A comparison of the dynamics of Malachite Green at the air/aqueous, alkane/aqueous and silica/aqueous interfaces, obtained by ultrafast second harmonic generation methods, indicates that the structure of water at the air/aqueous and alkane/aqueous interfaces is similar, in support of molecular simulations, but differ from that at the silica/aqueous interface. The dynamics are slower at all of these interfaces than in bulk water, by a factor of three to five in the case of the air/aqueous and alkane/aqueous interfaces, and almost an order of magnitude in the case of the silica/aqueous interface

(6.2 ps). The results suggest increased solvent structure and friction at the aqueous interface, with the silica/aqueous interface being the most structured.

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"Electron Photodetachment from Halide Ions in Solution: Excited State Dynamics in the Polarization Well"

Long, F. H.; Shi, X.; Lu, H; and Eissenthal K. B.

J. Phys. Chem., 98, 7252 (1994)

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Borguet, E.; Shi, X.; and Eissenthal, K. B.

"Second Harmonic and Sum Frequency Studies of Chemical Equilibria and Phase Transitions at Liquid Interfaces" in *Reaction Dynamics in Clusters and Condensed Phases*, eds., Jortner, J.; Levine, R. D.; and Pullman, B. Kluwer (Kluwer Academic Publishers, Dordrecht, Holland, 1994)

Eissenthal, K. B. and Gutow, J. H.

"Studies of Surface pKa and the Polarization of Water Molecules by a Long Chain Amine Monolayer at the Air/Aqueous Interface"

Wang, H.; Zhao, X.; and Eissenthal, K. B.

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"Studies of Orientational Fluctuations and Phase Transitions in Monolayers at the Air/Aqueous Interface by Second Harmonic Generation"

Zhao, X. and Eissenthal, K. B.

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"Liquid Interfaces"

Eissenthal, K. B.

Accts. Chem. Res., 26, 636 (1993)

"New Method for Determination of Surface pKa using Second Harmonic Generation"

Zhao, X.; Ong, S.; Wang, H.; and Eissenthal, K.B.

Chem. Phys. Lett., 214, 203 (1993)

"Sudden Structural Change at an Air/Binary Liquid Interface: Sum-Frequency Study of the Air/Acetonitrile-Water interface"

Zhang, D.; Gutow, J. H.; Eissenthal, K. B.; and Heinz, T. F.

J.Chem. Phys., 98, 5099 (1993)

"Polarization of Water Molecules at a Charged Interface: Second Harmonic Studies of Charged Monolayers at the Air/Water Interface"

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ed. W. Kaiser (Springer - Verlag, Berlin 1992)

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"Intensity Dependent Geminate Recombination in Water"

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Chem. Phys. Lett., 185, 47 (1991)

"Rotational Relaxation at the Air/Water Interface Studied by Time Resolved Second Harmonic Generation."

Castro, A.; Sitzmann, E.V.; Zhang, D.; and Eisenthal, K.B.

J. Phys. Chem., 95, 6752 (1991)

"Energetics of Adsorption of Neutral and Charged Molecules at the Air/Water Interface by Second Harmonic Generation - Hydrophobic and Solvation Effects"

Castro, A.; Bhattacharyya, K.; and Eisenthal, K.B.

J. Chem. Phys., 95, 1310 (1991)

"Orientational Fluctuations and Phase Transitions of Long Chain Molecules at the Air/Water Interface"

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